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**UTILITY PATENT  
APPLICATION TRANSMITTAL**

Only for new non-provisional applications under 37 CFR 1.53(b))  
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Attorney Docket No.	96047CIP (3600-011-02)	Total Pages	51
First Named Inventor or Application Identifier			
Angelos KYRLIDIS, Steven R. REZNEK, and James A. BELM			
Express Mail Label No. EL352565774US			

**APPLICATION ELEMENTS FOR:**  
CHROMATOGRAPHY AND OTHER ADSORPTIONS USING MODIFIED CARBON ADSORBENTS

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1.  Fee Transmittal Form (Incorporated within this form) Submit an original and a duplicate for fee processing)

2.  Application Total Pages [42]

3.  Drawing(s) (35 USC 113) (Figs. 1-6) Total Sheets [6]

4.  Oath or Declaration and Power of Attorney Total Pages [ ]  
 a.  Newly executed (original or copy)  
 b.  Copy from prior application (37 CFR 1.63(d)) (for continuation/divisional with Box 17 completed).  
 c.  Deletion of Inventor(s) Signed statement attached deleting inventor(s) named in prior application, see 37 CFR 1.63(d)(2) and 1.33(b).

5.  Incorporation by reference (useable if box 4b is checked)  
 The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein

6.  Microfiche Computer Program (Appendix)

7.  Nucleotide and/or Amino Acid Sequence Submission (if applicable, all necessary)  
 a.  Computer Readable Copy  
 b.  Paper Copy (identical to computer copy)  
 c.  Statement Verifying identity of above copies

**ACCOMPANYING APPLICATION PARTS**

8.  Assignment Papers (cover sheet and document(s)) Total Sheets [ ]  
 9.  37 CFR 3.73(b) Statement (when there is an assignee)

Date September 1, 2000 Label No. EL352565774US

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Attorney  
Docket No.

96047CIP (3600-011-02)

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Angelos KYRLIDIS, Steven R. REZNEK, and James A. BELMONT

**PAGE 2 OF 3**

10.  English translation Document (if applicable)

11.  Information Disclosure Statement  Copies of IDS Citations Total Pages

12.  Preliminary Amendment  Please cancel claims

13.  Return Receipt Postcard (MPEP 503)

14.  Small Entity Statement(s)  Statement filed in prior application

15.  Claim for Convention Priority  Certified copy of Priority Document(s)

a. Priority of application no. filed on is claimed under 35 USC 119.

The certified copies/copy have/has been filed in prior application Serial No.

(For Continuing Applications, if applicable)

16.  Other

17. If a CONTINUING APPLICATION, check appropriate box and supply the requisite information:

Continuation  Division  Continuation-in-part (CIP) of prior U.S. Application No. 09/475,385.

a.

Fee Transmittal The filing fee is calculated below	Number Filed	Number Extra	Rate	Basic Fee \$690.00
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Independent Claims	6 - 3	3	x \$78.00	\$234.00
Multiple Dependent Claims			\$260.00	
			Filing Fee	\$ 1,446.00
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Fee for recording enclosed Assignment			\$40.00	
TOTAL				\$1,446.00

UTILITY PATENT  
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Attorney Docket No.	96047CIP (3600-011-02)
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PAGE 3 OF 3	

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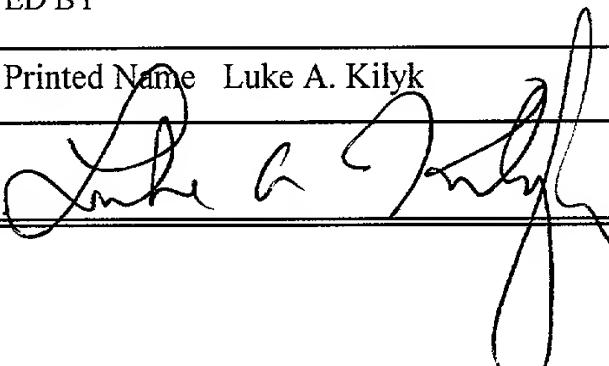
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Attorney Docket No. 96074CIP (3600-011-02)

U.S. PATENT APPLICATION

OF

Angelos KYRLIDIS, Steven R. REZNEK, and James A. BELMONT

FOR

CHROMATOGRAPHY AND OTHER ADSORPTIONS  
USING MODIFIED CARBON ADSORBENTS

CHROMATOGRAPHY AND OTHER ADSORPTIONS  
USING MODIFIED CARBON ADSORBENTS

This application is a continuation-in-part of U.S. Patent Application No. 09/475,385  
5 filed December 30, 1999, which is a continuation of U.S. Patent Application No. 08/663,709  
filed June 14, 1996, both are incorporated in their entireties by reference herein.

**FIELD OF THE INVENTION**

This invention relates to separation devices and processes as well as the use of modified  
10 carbonaceous materials as adsorbents and also relates to methods of using these adsorbents,  
including a method to increase the adsorption capacity and/or alter the adsorption affinity of  
carbonaceous materials capable of adsorbing an adsorbate.

**BACKGROUND OF THE INVENTION**

15 Adsorption is an important operation in many industrial processes. The effectiveness of  
an adsorbent depends, primarily, on its surface area, pore structure, and surface chemistry. The  
nature of the adsorbate which is to be adsorbed frequently dictates the chemical nature of the  
adsorbent. For example, carbonaceous adsorbents are often used to selectively remove organic  
compounds from liquid, gaseous, or vapor media. Silica and alumina based adsorbents are  
20 employed to selectively adsorb polar adsorbates such as water, ammonia, and the like from  
similar media.

The efficacy of an adsorbent for a particular application is usually determined by the  
adsorption capacity and selectivity of the adsorbent for the adsorbate in question. The  
adsorption capacity may be measured per unit mass or per unit volume of the adsorbent. In  
25 general, the higher the adsorption capacity and selectivity of an adsorbent for a particular

adsorbate, the more useful it is, since less of the adsorbent has to be used to effect the same removal of the adsorbate.

Carbonaceous materials, such as activated carbon, carbon black, and the like, represent an important class of adsorbents which are used in many fields such as separation, purification, 5 and waste treatment, among others. Because of their widespread use, any method for improving the adsorption properties of carbonaceous adsorbents for a particular adsorbate can have a large impact on the efficacy and economy of the processes utilizing them. Therefore, attempts have been made in the past to modify the surface chemistry of carbonaceous adsorbents. The methods employed for their modification can be broadly classified into physical and chemical 10 means. In surface modification by physical means, a species is deposited on the surface of the carbonaceous adsorbent to form a layer which then changes its adsorption properties. However, such modification techniques have limited utility because the deposited layer is easily removed. In surface modification by chemical means, the modifying species is attached to the carbon surface by a chemical bonding mechanism.

15 The characteristics of the adsorption isotherm, representing the relationship between the extent of adsorption and adsorbate concentration or adsorbate partial pressure at a fixed temperature, is also of importance. As described by Sircar et al. in "Activated Carbon for Gas Separation and Storage," *Carbon*, Vol. 34, No. 1, pp. 1-12 (1996), the characteristics of the preferred adsorption isotherm will depend on the separation process being employed. For 20 example, in cases where adsorbent regeneration is effected by a pressure swing, the preferred adsorbent is one with a moderate affinity for the adsorbate. When the adsorbate is strongly adsorbed, that is, when it has a strong affinity for the adsorbent, regeneration becomes difficult and energy intensive. On the other hand, when the adsorbent exhibits a weak affinity for the adsorbate, it has a small adsorption capacity at low adsorbent partial pressures and, hence, the 25 adsorption mass transfer zone becomes very long. Thus, the availability of a method for altering

the affinity of an adsorbent for an adsorbate is advantageous.

Thus, any method for increasing the adsorption capacity and/or modifying the adsorption affinity of the adsorbent enhances its usefulness in adsorption applications. As already noted, chemical modification can be used to alter the adsorptive properties of 5 carbonaceous adsorbents. The range of chemical species which can be attached, however, is limited.

Bansal, Donnet and Stoeckli (in Chapter 5 of Active Carbon, Marcel Dekker, Inc., 1988) have reviewed different techniques of carbon surface modification. Physical impregnation methods are described, as are methods that rely on chemical reactions with various species to 10 modify the surface of the carbon. Some of the chemical surface modification techniques described by Bansal et al. are oxidation, halogenation, sulfonation, and ammoniation. Several of these techniques require treatment of the carbon at elevated temperatures. Another technique involving oxidation of the carbon with  $\text{HNO}_3$  in the presence of a catalyst, has been described by Sircar and Golden (U.S. Patent No. 4,702,749). However, these techniques have certain 15 disadvantages apparent to those familiar with the field.

In chromatography and other separation methods, there is a certain amount of selectivity that is necessary in order for the stationary phase to separate the various components in a mixture. For this reason, carbon products, such as carbon black, graphite, and activated carbon, have not been used as a standard stationary phase in certain separation systems because carbon 20 is a strong non-specific adsorbent. This has been disappointing in the past, because carbon products, otherwise, would have many advantages over commercially available adsorbents. For instance, there are no corrosion problems with carbon products, which are stable at a wide pH range unlike silica particles which are stable only in the pH range of 1-8, nor are there any swelling problems with carbon products, which are stable in all organic solvents, unlike 25 polysaccharide-based chromatographic particles, which have solvent restrictions. In addition,

carbon products can be subjected to large temperature ranges and/or extreme pressures which would be beneficial for certain types of adsorptions, such as temperature swings used in some types of chromatography. In addition, with certain separation processes used in the production of biopharmaceuticals for clinical applications, the sterilization requirements or 5 recommendations provide for the use of hot sodium hydroxide. With such sterilization procedures, the current popular stationary phases such as silica columns, cannot be used. Further, the polymeric columns such as cellulose polymers, are chemically but not physically stable to such sterilization treatments.

Accordingly, there is a need to provide a new class of adsorbents and new separation 10 devices which can make use of carbon materials that have the advantages described above but are capable of being selective in their adsorption in order to serve as suitable adsorbents in separation processes such as chromatography.

### **SUMMARY OF THE INVENTION**

15 To achieve these and other advantages and in accordance with the purposes of the present invention, as embodied and broadly described herein, the present invention relates to an adsorbent composition containing a modified carbonaceous material capable of adsorbing an adsorbate.

The present invention also relates to a separation device having a mobile phase and a 20 stationary phase, wherein said stationary phase is a carbonaceous material having attached at least one organic group. The carbonaceous material having attached at least one organic group is capable of adsorbing one or more chemical species present in a mixture.

The present invention further relates to a chromatography column containing a column having a stationary phase and a mobile phase. The stationary phase is at least a carbonaceous 25 material having attached at least one organic group wherein the carbonaceous material having at

least one organic group is capable of adsorbing at least one chemical species present in a mixture.

The present invention further relates to a method for conducting chromatography on a substance and involves passing the substance through a column having a stationary phase and a mobile phase, wherein the stationary phase is at least a carbonaceous material having attached at least one organic group. The chromatography can be, for instance, a size exclusion chromatography, an affinity-type chromatography, an adsorption-desorption chromatography, or variations thereof or combinations thereof. Also, the chromatography can be a reverse phase chromatography, ion exchange chromatography, hydrophobic interaction chromatography, or chiral chromatography.

The present invention, in addition, relates to bioseparations using the chromatography methods described above.

The present invention also relates to separations using electrophoresis wherein the stationary phase is a carbonaceous material having attached at least one organic group.

The present invention further relates to a separation device containing a membrane wherein said membrane contains a carbonaceous material having attached at least one organic group.

The separation device can also be a magnetic separation device or a reverse osmosis device wherein the stationary phase or the membrane contains a carbonaceous material having attached at least one organic group.

Another embodiment of the present invention relates to a method to increase the adsorption capacity of a carbonaceous material capable of adsorbing an adsorbate or altering the adsorption isotherm of the adsorbate on the adsorbent, for instance, to allow an easier regeneration of the adsorbent. In this method, at least one organic group capable of increasing the adsorption capacity of a carbonaceous material is attached to the carbonaceous material.

The present invention, in addition, relates to a method of adsorbing an adsorbate and includes the step of contacting the adsorbate with a carbonaceous material which has been modified by attaching an organic group. The modified carbonaceous material is capable of adsorbing the adsorbate and at least one organic group is attached to the carbonaceous material.

5       Additional features and advantages of the present invention will be set forth in part in the description which follows, and in part will be apparent from the description, or may be learned by practice of the present invention. The objectives and other advantages of the present invention will be realized and attained by means of the elements and combinations particularly pointed out in the written description and appended claims.

10      It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are intended to provide further explanation of the present invention, as claimed.

15      The accompanying figures, which are incorporated in and constitute a part of this specification, illustrate several embodiments of the present invention and together with the description, serve to explain the principles of the present invention.

#### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1 is a graph plotting the amount of water adsorption on modified and unmodified carbon black.

20      Figure 2 is a graph plotting the amount of water adsorption on modified and unmodified activated carbon.

Figure 3 is a graph plotting the amount of water adsorption on modified and unmodified carbon black per unit surface area.

25      Figure 4 is a graph plotting the amount of water adsorption on modified and unmodified activated carbon per unit surface area.

Figure 5 is a graph plotting the amount of CO<sub>2</sub> adsorption on modified and unmodified carbon black at 273 K.

Figure 6 is a graph plotting the concentration of supernatant vs. the concentration of loaded Bovine Serum Albumin (BSA) solution in the presence of various carbonaceous materials.

#### **DETAILED DESCRIPTION OF THE PRESENT INVENTION**

The present invention relates to separation devices which typically have a stationary phase. The stationary phase, for purposes of the present invention, is a carbonaceous material having attached at least one organic group. This material is also known, once the organic group is attached, as a modified carbonaceous material for purposes of the present invention. The organic group is preferably attached (e.g., chemically) to the surfaces of the carbonaceous material, preferably by covalent bonds.

One preferred separation device is a chromatography column which, for purposes of the present invention, contains a column having a mobile phase and a stationary phase. The stationary phase is at least the modified carbonaceous material of the present invention. The mobile phase can be any conventional mobile phase used in the separation of chemical compounds or species from a mixture, such as solvents and the like. The present invention further relates to a method for conducting chromatography on a substance or mixture which involves passing the substance through a column packed with at least the modified carbonaceous material as the stationary phase and the mobile phase. The type of chromatography that can be accomplished by the present invention includes, but is not limited to, size exclusion chromatography and affinity chromatography (wherein the affinity between the modified carbonaceous material and the different chemical species in the mixture is different such that separation occurs at different rates). Another type of chromatography that can be

accomplished by the present invention is adsorption-desorption chromatography, reverse phase chromatography, ion exchange chromatography, hydrophobic interaction chromatography, chiral chromatography, capillary liquid chromatography, or electrochromatography.

Chromatographic separation of proteins and other biomolecules can also be  
5 accomplished by the present invention. An example of such a bioseparation would involve the use of a stationary phase wherein polyols or polyethylene glycol compounds are attached on the carbonaceous material. Another example of a bioseparation would involve the use of a stationary phase wherein benzoic acid or benzenesulfonic groups are attached to the surface of  
10 the carbonaceous material.

10 Typically, a chromatographic system contains a mobile phase, a stationary phase, a pumping system, and a detector. Generally, the stationary phase contains insoluble particles which are preferably spherical and preferably range in size from about 1 micron to about 500 microns. These particles have a surface area ranging from about 1 to about 500 m<sup>2</sup>/g and a mean pore diameter ranging from about 20 to about 20,000 Angstrom. The choice of these particles  
15 depends on the physical, chemical, and/or biological interactions that need to be exploited by the separation. Certain functional groups on conventional stationary phases, such as silica, agarose, polystyrene-divinylbenzene, polyacrylamide, dextrin, hydroxyapatite, cross-linked polysaccharides, and polymethacrylates are functionalized with certain groups in order to accomplish the selective separation of particular chemical compounds from a mixture. The  
20 precise functional groups that accomplish this desired specification are set forth, for instance, in Garcia, Bonen et al., *"Bioseparation Process Science,"* Blackwell Science (1999), incorporated in its entirety by reference herein. In preferred instances, the functional groups described in Garcia et al. is the organic group attached to the carbonaceous materials based on the present invention or are part of the organic group attached to the carbonaceous materials (e.g., the  
25 functional groups of Garcia et al. attached to the carbonaceous material through at least one

aromatic group or alkyl group, wherein the aromatic group or alkyl group are preferably directly attached to the carbonaceous material).

Another form of separation is electrophoresis which uses an applied electric field to produce directed movement of charged molecules. The process is similar to chromatographic methods in that a fixed barrier phase or stationary phase is used to facilitate separation. In the present invention, electrophoresis can be accomplished by using a stationary phase which contains the modified carbonaceous material of the present invention.

Similarly, magnetic separations, such as magnetic bioseparations, can be accomplished using the modified magnetic carbonaceous materials of the present invention as the stationary phase.

In addition, membrane separations, such as reverse osmosis, can be accomplished by forming the membrane such that it contains modified carbonaceous materials. The membrane can be formed by dispersing the modified carbonaceous material in a polymer and casting the polymer mixture to form a membrane. Another way to make the membrane is to form a conventional membrane and then surface modify the membrane to attach organic groups onto the membrane. Membranes can be used in a variety of separation techniques, including protein separations and/or metal removal.

Generally, any separation technique which involves the use of a stationary phase can be improved by the present invention. In particular, the stationary phase can be or can contain the modified carbonaceous material of the present invention. Upon knowing the desired chemical compound or species to be separated, the modified carbonaceous material can be tailored to be selective to the targeted chemical species by attaching an organic group or organic groups onto the carbonaceous material to suit the separation needed. Since many functional groups are known to cause particular selectivity in separations, these groups can be attached onto the carbonaceous material to form the modified carbonaceous material of the present invention and

achieve the desired selectivity for separation processes.

In one embodiment, an adsorbent composition of the present invention contains a modified carbonaceous material capable of adsorbing an adsorbate wherein at least one organic group is attached to the carbonaceous material.

5        The carbonaceous material capable of adsorbing an adsorbate includes, but is not limited to, activated carbon, carbon black, graphite, or other carbonaceous material obtained by the pyrolysis of cellulosic, fuel oil, polymeric, or other precursors. Additional examples, include but are not limited to, carbon fibers, carbon cloth, vitreous carbon, carbon aerogels, pyrolyzed ion exchange resins, pyrolyzed polymer resins, mesoporous carbon microbeads, pelleted carbon  
10      powder, nanotubes, buckyballs, silicon-treated carbon black, silica-coated carbon black, metal-treated carbon black, densified carbon black, carbon clad silica, alumina, and ceria particles, and combinations thereof or activated versions thereof. The carbonaceous material can also be a waste product or by-product of carbonaceous material obtained by pyrolysis. Preferably, the carbonaceous material is activated carbon or carbon black capable of adsorbing an adsorbate.  
15      Commercial examples of carbon black include, but are not limited to, Black Pearls® 2000 carbon black, Black Pearls® 430 carbon black, Black Pearls® 900 carbon black, and Black Pearls® 120 carbon black, all available from Cabot Corporation. Commercial examples of activated carbon include Darco S51, available from Norit; Sorbonorit 3, available from Norit; Ambersorb adsorbent; Hypercarb carbon particle; TosoHaas carbon materials; and BPL  
20      activated carbon from Calgon. The carbonaceous material modified by the procedures described herein may be a microporous or mesoporous activated carbon in granular or pellet form; a carbon black of different structures in fluffy or pelleted form; or any other carbonaceous material whose applicability to this invention is apparent to those skilled in the art, such as carbon fibers or carbon cloth. The choice of carbonaceous material used eventually depends on  
25      a variety of different factors, including the application for which it is intended. Each of these

types of carbonaceous material has the ability to adsorb at least one adsorbate. A variety of BET surface areas, micropore volumes, and total pore volumes are available depending on the desired end use of the carbonaceous material.

Carbonaceous materials include, but are not limited to, material obtained by the 5 compaction of small carbon particles and other finely divided forms of carbon as long as the carbon has the ability to adsorb at least one adsorbate and is capable of being chemically modified in accordance with the present invention.

Also, for purposes of the present invention, the carbonaceous material can be an aggregate comprising a carbon phase and a silicon-containing species phase. A description of 10 this aggregate as well as means of making this aggregate is described in PCT Publication No. WO 96/37547 and WO 98/47971 as well as U.S. Patent Nos. 5,830,930; 5,869,550; 5,877,238; 5,919,841; 5,948,835; and 5,977,213. All of these patents and publications are hereby incorporated in their entireties herein by reference.

The carbonaceous material for purposes of the present invention, can also be an 15 aggregate comprising a carbon phase and metal-containing species phase where the metal-containing species phase can be a variety of different metals such as magnesium, calcium, titanium, vanadium, cobalt, nickel, zirconium, tin, antimony, chromium, neodymium, lead, tellurium, barium, cesium, iron, molybdenum, aluminum, and zinc, and mixtures thereof. The aggregate comprising the carbon phase and a metal-containing species phase is described in 20 U.S. Patent No. 6,017,980, also hereby incorporated in its entirety herein by reference.

Also, for purposes of the present invention, the carbonaceous material includes a silica-coated carbon black, such as that described in U.S. Patent No. 5,916,934 and PCT Publication No. WO 96/37547, published November 28, 1996, also hereby incorporated in their entirety herein by reference.

The carbonaceous material described above is then modified by the attachment of an organic group to the carbonaceous material. Preferred processes for attaching an organic group to a carbonaceous material and examples of organic groups are described in detail in U.S. Patent Nos. 5,554,739; 5,559,169; 5,571,311; 5,575,845; 5,630,868; 5,672,198; 5,698,016; 5,837,045; 5,922,118; 5,968,243; 6,042,643; 5,900,029; 5,955,232; 5,895,522; 5,885,335; 5,851,280; 5,803,959; 5,713,988; and 5,707,432; and International Patent Publication Nos. WO 97/47691; WO 99/23174; WO 99/31175; WO 99/51690; WO 99/63007; and WO 00/22051; all incorporated in their entirety by reference herein. These processes can be preferably used in preparing the modified carbon adsorbents of the present invention and permit the attachment of an organic group to the carbonaceous material via a chemical reaction. As indicated above, the organic group attached to the carbonaceous material is one preferably capable of increasing the adsorption capacity and/or selectivity of the carbonaceous material and/or enhancing the resolution of solute peaks in chromatographic separations.

As indicated above, once the desired separation technique is chosen and the particular chemical species preferably known, a particular functional group or multiple functional groups can be chosen to be attached onto the carbonaceous material in order to accomplish the selectivity needed to conduct the separation process. For instance, as set forth in Garcia et al., heparin is used in the separation of lipoproteins, accordingly, heparin can be attached onto carbonaceous material in order to accomplish the desired separation. Similarly, when cationic exchange processes are needed, a sulfonic acid, for instance, can be attached on a carbonaceous material and when anionic exchanges are needed, a quaternary amine can be attached onto the carbonaceous material. Thus, with the present invention, and the knowledge possessed by one skilled in the art, separation techniques can be conducted using modified carbonaceous material to achieve the selectivity desired.

Thus, the present invention provides a carbonaceous material which is resistant to corrosion, swelling, and/or extreme temperatures and pressures, but also provides the desired selectivity. In essence, the present invention gives the separation field the best of both worlds, namely, selectivity combined with a resilient stationary phase.

5 A preferred process for attaching an organic group to the carbonaceous materials involves the reaction of at least one diazonium salt with a carbonaceous material in the absence of an externally applied current sufficient to reduce the diazonium salt. That is, the reaction between the diazonium salt and the carbonaceous material proceeds without an external source 10 of electrons sufficient to reduce the diazonium salt. Mixtures of different diazonium salts may be used. This process can be carried out under a variety of reaction conditions and in any type 15 of reaction medium, including both protic and aprotic solvent systems or slurries.

In another preferred process, at least one diazonium salt reacts with a carbonaceous material in a protic reaction medium. Mixtures of different diazonium salts may be used in this process. This process can also be carried out under a variety of reaction conditions.

15 Preferably, in both processes, the diazonium salt is formed *in situ*. If desired, in either process, the modified carbonaceous material can be isolated and dried by means known in the art. Furthermore, the modified carbonaceous material can be treated to remove impurities by known techniques. The various preferred embodiments of these processes are discussed below.

The processes can be carried out under a wide variety of conditions and in general are 20 not limited by any particular condition. The reaction conditions must be such that the particular diazonium salt is sufficiently stable to allow it to react with the carbonaceous material. Thus, the processes can be carried out under reaction conditions where the diazonium salt is short lived. The reaction between the diazonium salt and the carbonaceous material occurs, for 25 example, over a wide range of pH and temperature. The processes can be carried out at acidic, neutral, and basic pH. Preferably, the pH ranges from about 1 to 9. The reaction temperature

may preferably range from 0°C to 100°C.

Diazonium salts, as known in the art, may be formed for example by the reaction of primary amines with aqueous solutions of nitrous acid. A general discussion of diazonium salts and methods for their preparation is found in Morrison and Boyd, Organic Chemistry, 5th Ed., 5 pp. 973-983, (Allyn and Bacon, Inc. 1987) and March, Advanced Organic Chemistry: Reactions, Mechanisms, and Structures, 4th Ed., (Wiley, 1992). According to this invention, a diazonium salt is an organic compound having one or more diazonium groups.

The diazonium salt may be prepared prior to reaction with the carbonaceous material or, more preferably, generated *in situ* using techniques known in the art. *In situ* generation also 10 allows the use of unstable diazonium salts such as alkyl diazonium salts and avoids unnecessary handling or manipulation of the diazonium salt. In particularly preferred processes, both the nitrous acid and the diazonium salt are generated *in situ*.

A diazonium salt, as is known in the art, may be generated by reacting a primary amine, a nitrite and an acid. The nitrite may be any metal nitrite, preferably lithium nitrite, sodium 15 nitrite, potassium nitrite, or zinc nitrite, or any organic nitrite such as for example isoamyl nitrite or ethyl nitrite. The acid may be any acid, inorganic or organic, which is effective in the generation of the diazonium salt. Preferred acids include nitric acid, HNO<sub>3</sub>, hydrochloric acid, HCl, and sulfuric acid, H<sub>2</sub>SO<sub>4</sub>.

The diazonium salt may also be generated by reacting the primary amine with an 20 aqueous solution of nitrogen dioxide. The aqueous solution of nitrogen dioxide, NO<sub>2</sub>/H<sub>2</sub>O, provides the nitrous acid needed to generate the diazonium salt.

Generating the diazonium salt in the presence of excess HCl may be less preferred than other alternatives because HCl is corrosive to stainless steel. Generation of the diazonium salt with NO<sub>2</sub>/H<sub>2</sub>O has the additional advantage of being less corrosive to stainless steel or other 25 metals commonly used for reaction vessels. Generation using H<sub>2</sub>SO<sub>4</sub>/NaNO<sub>2</sub> or HNO<sub>3</sub>/NaNO<sub>2</sub>

are also relatively non-corrosive.

In general, generating a diazonium salt from a primary amine, a nitrite, and an acid requires two equivalents of acid based on the amount of amine used. In an *in situ* process, the diazonium salt can be generated using one equivalent of the acid. When the primary amine 5 contains a strong acid group, adding a separate acid may not be necessary. The acid group or groups of the primary amine can supply one or both of the needed equivalents of acid. When the primary amine contains a strong acid group, preferably either no additional acid or up to one equivalent of additional acid is added to a process of the invention to generate the diazonium salt *in situ*. A slight excess of additional acid may be used. One example of such a primary 10 amine is para-aminobenzenesulfonic acid (sulfanilic acid).

In general, diazonium salts are thermally unstable. They are typically prepared in solution at low temperatures, such as 0-5°C, and used without isolation of the salt. Heating solutions of some diazonium salts may liberate nitrogen and form either the corresponding alcohols in acidic media or the organic free radicals in basic media.

15 However, the diazonium salt need only be sufficiently stable to allow reaction with the carbonaceous material. Thus, the processes can be carried out with some diazonium salts otherwise considered to be unstable and subject to decomposition. Some decomposition processes may compete with the reaction between the carbonaceous material and the diazonium salt and may reduce the total number of organic groups attached to the carbonaceous material.

20 Further, the reaction may be carried out at elevated temperatures where many diazonium salts may be susceptible to decomposition. Elevated temperatures may also advantageously increase the solubility of the diazonium salt in the reaction medium and improve its handling during the process. However, elevated temperatures may result in some loss of the diazonium salt due to other decomposition processes.

Reagents can be added to form the diazonium salt *in situ*, to a suspension of carbonaceous material in the reaction medium, *for example*, water. Thus, a carbonaceous material suspension to be used may already contain one or more reagents to generate the diazonium salt and the process accomplished by adding the remaining reagents.

5       Reactions to form a diazonium salt are compatible with a large variety of functional groups commonly found on organic compounds. Thus, only the availability of a diazonium salt for reaction with a carbonaceous material limits the processes of the invention.

The processes can be carried out in any reaction medium which allows the reaction between the diazonium salt and the carbonaceous material to proceed. Preferably, the reaction 10 medium is a solvent-based system. The solvent may be a protic solvent, an aprotic solvent, or a mixture of solvents. Protic solvents are solvents, like water or methanol, containing a hydrogen attached to an oxygen or nitrogen and thus are sufficiently acidic to form hydrogen bonds. Aprotic solvents are solvents which do not contain an acidic hydrogen as defined above. Aprotic solvents include, for example, solvents such as hexanes, tetrahydrofuran (THF), 15 acetonitrile, and benzonitrile. For a discussion of protic and aprotic solvents see Morrison and Boyd, Organic Chemistry, 5th Ed., pp. 228-231, (Allyn and Bacon, Inc. 1987).

The processes are preferably carried out in a protic reaction medium, that is, in a protic solvent alone or a mixture of solvents which contains at least one protic solvent. Preferred protic media include, but are not limited to water, aqueous media containing water and other 20 solvents, alcohols, and any media containing an alcohol, or mixtures of such media.

The reaction between a diazonium salt and a carbonaceous material can take place with any type of carbonaceous material, for example, in finely divided state or pelleted form. In one embodiment designed to reduce production costs, the reaction occurs during a process for forming carbonaceous material pellets. For example, a carbonaceous material product of the 25 invention can be prepared in a dry drum by spraying a solution or slurry of a diazonium salt onto

a carbonaceous material. Alternatively, the carbonaceous material product can be prepared by palletizing a carbonaceous material in the presence of a solvent system, such as water, containing the diazonium salt or the reagents to generate the diazonium salt *in situ*. Aqueous solvent systems are preferred.

5 In general, the processes produce inorganic by-products, such as salts. In some end uses, such as those discussed below, these by-products may be undesirable. Several possible ways to produce a carbonaceous material product without unwanted inorganic by-products or salts are as follows:

10 First, the diazonium salt can be purified before use by removing the unwanted inorganic by-product using means known in the art. Second, the diazonium salt can be generated with the use of an organic nitrite as the diazotization agent yielding the corresponding alcohol rather than an inorganic salt. Third, when the diazonium salt is generated from an amine having an acid group and aqueous  $\text{NO}_2$ , no inorganic salts are formed. Other ways may be known to those of skill in the art.

15 In addition to the inorganic by-products, the process may also produce organic by-products. They can be removed, for example, by extraction with organic solvents. Other ways of obtaining products without unwarranted organic by-products may be known to those of skill in the art, and include washing or removal of ions by reverse osmosis.

20 The reaction between a diazonium salt and a carbonaceous material forms a carbonaceous material product having an organic group attached to the carbonaceous material. The diazonium salt may contain the organic group to be attached to the carbonaceous material. It may be possible to produce the carbonaceous material products of this invention by other means known to those skilled in the art.

25 The organic group may be an aliphatic group, a cyclic organic group, or an organic compound having an aliphatic portion and a cyclic portion. As discussed above, the diazonium

salt employed can be derived from a primary amine having one of these groups and being capable of forming, even transiently, a diazonium salt. The organic group may be substituted or unsubstituted, branched or unbranched. Aliphatic groups include, for example, groups derived from alkanes, alkenes, alcohols, ethers, aldehydes, ketones, carboxylic acids, and carbohydrates.

5 Cyclic organic groups include, but are not limited to, alicyclic hydrocarbon groups (*for example*, cycloalkyls, cycloalkenyls), heterocyclic hydrocarbon groups (*for example*, pyrrolidinyl, pyrrolinyl, piperidinyl, morpholinyl, and the like), aryl groups (*for example*, phenyl, naphthyl, anthracenyl, and the like), and heteroaryl groups (imidazolyl, pyrazolyl, pyridinyl, thienyl, thiazolyl, furyl, indolyl, and the like). As the steric hindrance of a substituted organic group  
10 increases, the number of organic groups attached to the carbonaceous material from the reaction between the diazonium salt and the carbonaceous material may be diminished.

When the organic group is substituted, it may contain any functional group compatible with the formation of a diazonium salt. Functional groups include, but are not limited to, R, OR, COR, COOR, OCOR, carboxylate salts such as COOLi, COONa, COOK, COO<sup>-</sup>NR<sub>4</sub><sup>+</sup>,  
15 halogen, CN, NR<sub>2</sub>, SO<sub>3</sub>H, sulfonate salts such as SO<sub>3</sub>Li, SO<sub>3</sub>Na, SO<sub>3</sub>K, SO<sub>3</sub>NR<sub>4</sub><sup>+</sup>, OSO<sub>3</sub>H, OSO<sub>3</sub><sup>-</sup> salts, NR(COR), CONR<sub>2</sub>, NO<sub>2</sub>, PO<sub>3</sub>H<sub>2</sub>, phosphonate salts such as PO<sub>3</sub>HNa and PO<sub>3</sub>Na<sub>2</sub>, phosphate salts such as OPO<sub>3</sub>HNa and OPO<sub>3</sub>Na<sub>2</sub>, N=NR, NR<sub>3</sub><sup>+</sup>X<sup>-</sup>, PR<sub>3</sub><sup>+</sup>X<sup>-</sup>, S<sub>k</sub>R, SSO<sub>3</sub>H, SSO<sub>3</sub><sup>-</sup> salts, SO<sub>2</sub>NRR', SO<sub>2</sub>SR, SNRR', SNQ, SO<sub>2</sub>NQ, CO<sub>2</sub>NQ, S-(1,4-piperazinediyl)-SR, 2-(1,3-dithianyl) 2-(1,3-dithiolanyl), SOR, and SO<sub>2</sub>R. R and R', which can be the same or different,  
20 are independently hydrogen, branched or unbranched C<sub>1</sub>-C<sub>20</sub> substituted or unsubstituted, saturated or unsaturated hydrocarbon, e.g., alkyl, alkenyl, alkynyl, substituted or unsubstituted aryl, substituted or unsubstituted heteroaryl, substituted or unsubstituted alkylaryl, or substituted or unsubstituted arylalkyl. The integer k ranges from 1-8 and preferably from 2-4. The anion X<sup>-</sup> is a halide or an anion derived from a mineral or organic acid. Q is (CH<sub>2</sub>)<sub>w</sub>, (CH<sub>2</sub>)<sub>x</sub>O(CH<sub>2</sub>)<sub>z</sub>,  
25 (CH<sub>2</sub>)<sub>x</sub>NR(CH<sub>2</sub>)<sub>z</sub>, or (CH<sub>2</sub>)<sub>x</sub>S(CH<sub>2</sub>)<sub>z</sub>, where w is an integer from 2 to 6 and x and z are integers

from 1 to 6. In the above formula, specific examples of R and R' are  $\text{NH}_2\text{-C}_6\text{H}_4\text{-}$ ,  $\text{CH}_2\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$ ,  $\text{CH}_2\text{-C}_6\text{H}_4\text{-NH}_2$ , and  $\text{C}_6\text{H}_5$ .

Another example of an organic group is an aromatic group of the formula  $\text{A}_y\text{Ar-}$ , which corresponds to a primary amine of the formula  $\text{A}_y\text{ArNH}_2$ . In this formula, the variables have the following meanings: Ar is an aromatic radical such as an aryl or heteroaryl group. Ar can be selected from the group consisting of phenyl, naphthyl, anthracenyl, phenanthrenyl, biphenyl, pyridinyl, benzothiadiazolyl, and benzothiazolyl; A is a substituent on the aromatic radical independently selected from a preferred functional group described above or A is a linear, branched or cyclic hydrocarbon radical (preferably containing 1 to 20 carbon atoms), unsubstituted or substituted with one or more of those functional groups; and y is an integer from 1 to the total number of -CH radicals in the aromatic radical. For instance, y is an integer from 1 to 5 when Ar is phenyl, 1 to 7 when Ar is naphthyl, 1 to 9 when Ar is anthracenyl, phenanthrenyl, or biphenyl, or 1 to 4 when Ar is pyridinyl.

Another set of organic groups which may be attached to the carbonaceous material are organic groups substituted with an ionic or an ionizable group as a functional group. An ionizable group is one which is capable of forming an ionic group in the medium of use. The ionic group may be an anionic group or a cationic group and the ionizable group may form an anion or a cation.

Ionizable functional groups forming anions include, for example, acidic groups or salts of acidic groups. The organic groups, therefore, include groups derived from organic acids. Preferably, when it contains an ionizable group forming an anion, such an organic group has a) an aromatic group or a  $\text{C}_1\text{-C}_{12}$  alkyl group and b) at least one acidic group having a pKa of less than 11, or at least one salt of an acidic group having a pKa of less than 11, or a mixture of at least one acidic group having a pKa of less than 11 and at least one salt of an acidic group having a pKa of less than 11. The pKa of the acidic group refers to the pKa of the organic group

as a whole, not just the acidic substituent. More preferably, the pKa is less than 10 and most preferably less than 9. Preferably, the aromatic group or the C<sub>1</sub>-C<sub>12</sub> alkyl group of the organic group is directly attached to the carbonaceous material. The aromatic group may be further substituted or unsubstituted, for example, with alkyl groups. The organic group can be a phenyl 5 or a naphthyl group and the acidic group is a sulfonic acid group, a sulfinic acid group, a phosphonic acid group, or a carboxylic acid group. Examples of these acidic groups and their salts are discussed above. The organic group can be a substituted or unsubstituted sulfophenyl 10 group or a salt thereof; a substituted or unsubstituted (polysulfo)phenyl group or a salt thereof; a substituted or unsubstituted sulfonaphthyl group or a salt thereof; or a substituted or unsubstituted (polysulfo)naphthyl group or a salt thereof. An example of a substituted 15 sulfophenyl group is hydroxysulfophenyl group or a salt thereof.

Specific organic groups having an ionizable functional group forming an anion (and their corresponding primary amines for use in a process according to the invention) are p-sulfophenyl (p-sulfanilic acid), 4-hydroxy-3-sulfophenyl (2-hydroxy-5-amino-benzenesulfonic acid), and 2-sulfoethyl (2-aminoethanesulfonic acid). 15

Amines represent examples of ionizable functional groups that form cationic groups. For example, amines may be protonated to form ammonium groups in acidic media. Preferably, an organic group having an amine substituent has a pK<sub>b</sub> of less than 5. Quaternary ammonium 20 groups (-NR<sub>3</sub><sup>+</sup>) and quaternary phosphonium groups (-PR<sub>3</sub><sup>+</sup>) also represent examples of cationic groups. The organic group can contain an aromatic group such as a phenyl or a naphthyl group and a quaternary ammonium or a quaternary phosphonium group. The aromatic group is preferably directly attached to the carbonaceous material. Quaternized cyclic amines, and even 25 quaternized aromatic amines, can also be used as the organic group. Thus, N-substituted pyridinium compounds, such as N-methyl-pyridyl, can be used in this regard. Examples of organic groups include, but are not limited to, (C<sub>5</sub>H<sub>4</sub>N)C<sub>2</sub>H<sub>5</sub><sup>+</sup>X<sup>-</sup>, C<sub>6</sub>H<sub>4</sub>(NC<sub>5</sub>H<sub>5</sub>)<sup>+</sup>X<sup>-</sup>,

$C_6H_4COCH_2N(CH_3)_3^+X^-$ ,  $C_6H_4COCH_2(NC_5H_5)^+X^-$ ,  $(C_5H_4N)CH_3^+X^-$ , and  $C_6H_4CH_2N(CH_3)_3^+X^-$ , where  $X^-$  is a halide or an anion derived from a mineral or organic acid.

Aromatic sulfides encompass another group of organic groups. These aromatic sulfides can be represented by the formulas  $Ar(CH_2)_qS_k(CH_2)_rAr'$  or  $A-(CH_2)_qS_k(CH_2)_rAr''$  wherein Ar and Ar' are independently substituted or unsubstituted arylene or heteroarylene groups, Ar'' is an aryl or heteroaryl group, k is 1 to 8 and q and r are 0-4. Substituted aryl groups would include substituted alkylaryl groups. Examples of arylene groups include phenylene groups, particularly p-phenylene groups, or benzothiazolylene groups. Aryl groups include phenyl, naphthyl and benzothiazolyl. The number of sulfurs present, defined by k preferably ranges from 2 to 4.

10 Examples of carbonaceous material products are those having an attached aromatic sulfide organic group of the formula  $-(C_6H_4)-S_k-(C_6H_4)-$ , where k is an integer from 1 to 8, and more preferably where k ranges from 2 to 4. Other examples of aromatic sulfide groups are bis-para- $(C_6H_4)-S_2-(C_6H_4)-$  and para- $(C_6H_4)-S_2-(C_6H_5)$ . The diazonium salts of these aromatic sulfide groups may be conveniently prepared from their corresponding primary amines,  $H_2N-Ar-S_k-Ar'-NH_2$  or  $H_2N-Ar-S_k-Ar''$ . Groups include dithiodi-4,1-phenylene, tetrathiodi-4,1-phenylene, phenyldithiophenylene, dithiodi-4,1-(3-chlorophenylene),  $-(4-C_6H_4)-S-S-(2-C_7H_4NS)$ ,  $-(4-C_6H_4)-S-S-(4-C_6H_4)-OH$ ,  $-6-(2-C_7H_3NS)-SH$ ,  $-(4-C_6H_4)-CH_2CH_2-S-S-CH_2CH_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2CH_2-S-S-CH_2CH_2-(4-C_6H_4)-$ ,  $-(2-C_6H_4)-S-S-(2-C_6H_4)-$ ,  $-(3-C_6H_4)-S-S-(3-C_6H_4)-$ ,  $-(6-C_6H_3N_2S)$ ,  $-6-(2-C_7H_3NS)-S-NRR'$  where RR' is  $-CH_2CH_2OCH_2CH_2-$ ,  $-(4-C_6H_4)-S-S-S-S-$   $(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH=CH_2$ ,  $-(4-C_6H_4)-S-SO_3H$ ,  $-(4-C_6H_4)-SO_2NH-(4-C_6H_4)-S-S-(4-C_6H_4)-NHSO_2-(4-C_6H_4)-$ ,  $-6-(2-C_7H_3NS)-S-S-2-(6-C_7H_3NS)-$ ,  $-(4-C_6H_4)-S-CH_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-SO_2-S-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2-S-CH_2-(4-C_6H_4)-$ ,  $-(3-C_6H_4)-CH_2-S-CH_2-(3-C_6H_4)-$ ,  $-(4-C_6H_4)-CH_2-S-S-CH_2-(4-C_6H_4)-$ ,  $-(3-C_6H_4)-CH_2-S-S-CH_2-(3-C_6H_4)-$ ,  $-(4-C_6H_4)-S-NRR'$ , where RR' is  $-CH_2CH_2OCH_2CH_2-$ ,  $-(4-C_6H_4)-SO_2NH-CH_2CH_2-S-S-CH_2CH_2-NHSO_2-(4-C_6H_4)-$ ,  $-(4-C_6H_4)-2-(1,3-dithianyl)$ , and  $-(4-C_6H_4)-S-(1,4-piperizinediyl)-S-(4-C_6H_4)-$ .

Another set of organic groups which may be attached to the carbonaceous material are organic groups having an aminophenyl, such as  $(C_6H_4)-NH_2$ ,  $(C_6H_4)-CH_2-(C_6H_4)-NH_2$ ,  $(C_6H_4)-SO_2-(C_6H_4)-NH_2$ .

Preferably, the organic group is a  $C_1-C_{100}$  alkyl group (more preferably a  $C_1-C_{12}$  alkyl group), an aromatic group, or other organic group, monomeric group, or polymeric group, each optionally having a functional group or ionic or ionizable group. More preferably, these groups are directly attached to the carbonaceous material.

The polymeric group can be any polymeric group capable of being attached to a carbon product. The polymeric group can be a polyolefin group, a polystyrenic group, a polyacrylate group, a polyamide group, a polyester group, or mixtures thereof. Monomeric groups are monomeric versions of the polymeric groups.

The organic group can also be an olefin group, a styrenic group, an acrylate group, an amide group, an ester, or mixtures thereof. The organic group can also be an aromatic group or an alkyl group, either group with an olefin group, a styrenic group, an acrylate group, an amide group, an ester group, or mixtures thereof, wherein preferably the aromatic group, or the alkyl group, like a  $C_1-C_{12}$  group, is directly attached to the carbon product.

The polymeric group can include an aromatic group or an alkyl group, like a  $C_1-C_{12}$  group, either group with a polyolefin group, a polystyrenic group, a polyacrylate group, a polyamide group, an polyester group, or mixtures thereof.

The organic group can also comprise an aralkyl group or alkylaryl group, which is preferably directly attached to the carbon product. Other examples of organic groups include a  $C_1-C_{100}$  alkyl group, and more preferably a  $C_{20}-C_{60}$  alkyl group.

Examples of other organic groups are organic groups having the following formulas (hyphens on one or more ends represents an attachment to a carbon product or to another group):

- Ar-CO<sub>2</sub>(C<sub>m</sub>H<sub>2m+1</sub>), where m = 0 to about 20;
- Ar-(C<sub>n</sub>H<sub>2n+1</sub>), where n = 1 to about 50;
- Ar-C<sub>p</sub>H<sub>2p</sub> Ar-, where p = 1 to about 10;
- Ar-CX<sub>3</sub>, where X is a halogen atom;
- 5 -Ar-O-CX<sub>3</sub>, where X is a halogen atom;
- Ar-SO<sub>3</sub><sup>-</sup>;
- Ar-SO<sub>2</sub>(C<sub>q</sub>H<sub>2q-1</sub>), where q = about 2 to about 10;
- Ar-S<sub>2</sub>-Ar-NH<sub>2</sub>;
- Ar-S<sub>2</sub>-Ar-;
- 10 -ArSO<sub>2</sub>H;
- Ar-((C<sub>n</sub>H<sub>2n</sub>)COOX)<sub>m</sub>, where n=0 to 20, m=1 to 3, and X=H, cations, or organic group; These groups are further activated and/or reacted with such groups as carbodiimides and further reacted with NH<sub>2</sub>-terminated functionalization groups; SOCl<sub>2</sub>, or PCl<sub>3</sub>, or PCl<sub>5</sub> to be converted to -Ar-(C<sub>n</sub>H<sub>2n</sub>)COCl)<sub>m</sub> groups and further reacted with OH-terminated 15 functionalization groups.
- Ar-((C<sub>n</sub>H<sub>2n</sub>)OH)<sub>m</sub>, where n=0 to 20, m=1 to 3; These groups are further activated and/or reacted with such groups as tosyl chloride and subsequently reacted with amino-terminated ligands; carbonyldiimidazole and subsequently reacted with amino-terminated ligands; carbonylchloride terminated ligands; and epoxy terminated ligands.
- 20 -Ar-((C<sub>n</sub>H<sub>2n</sub>)NH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3, and its protonated form: -Ar-((C<sub>n</sub>H<sub>2n</sub>)NH<sub>3</sub>X)<sub>m</sub>, where X is an ion; These groups are further activated and/or reacted with such groups as carbodiimide activated carboxyl-terminated ligands; carbonyldiimidazole activated hydroxy-terminated ligands; tosyl activated hydroxy-terminated ligands; vinyl terminated ligands; alkylhalide terminated ligands; or epoxy terminated ligands.

-Ar-((C<sub>n</sub>H<sub>2n</sub>)CHNH<sub>3</sub><sup>+</sup>COO<sup>-</sup>)<sub>m</sub> where n=0 to 20 and m=1 to 3; These groups are derivatized further by reaction through the carboxylic group by reaction with NH<sub>2</sub> or OH terminated groups or through the amino group by reaction with activated carboxy-terminated ligands, activated hydroxy-terminated ligands, vinyl ligands, alkylhalide terminated ligands, 5 or epoxy terminated ligands.

-Ar-((C<sub>n</sub>H<sub>2n</sub>)CH=CH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3 or -Ar-((C<sub>n</sub>H<sub>2n</sub>)SO<sub>2</sub>CH=CH<sub>2</sub>)<sub>m</sub>, where n=0 to 20, m=1 to 3. These groups are further activated and/or reacted with such groups as amino-terminated ligands; peroxy-acids to form epoxides and subsequently reacted with hydroxy- or amino-terminated ligands; hydrogen halides to form - 10 Ar((C<sub>n</sub>H<sub>2n</sub>)CH<sub>2</sub>CH<sub>2</sub>X)<sub>m</sub> groups and subsequently reacted with amino-terminated ligands. or mixtures thereof. Other reaction schemes can be used to form various groups onto the carbonaceous material.

Preferred mixtures of organic groups include the following:

-Ar-SO<sub>3</sub><sup>-</sup> and -Ar(C<sub>n</sub>H<sub>2n+1</sub>), where n = 1 to about 50; 15 -Ar-S<sub>2</sub>-Ar-NH<sub>2</sub> and -ArC<sub>p</sub>H<sub>2p</sub>Ar-, where p = 1 to about 10; -Ar-S<sub>2</sub>-Ar- and -ArC<sub>p</sub>H<sub>2p</sub>Ar-, where p = 1 to about 10; or at least two different -Ar-CO<sub>2</sub>(C<sub>m</sub>H<sub>2m+1</sub>), where m = 0 to about 20.

The various organic, monomeric, and polymeric groups described above and below which are part of the modified carbon product can be unsubstituted or substituted and can be 20 branched or linear.

Any one or more of these organic groups, after attachment to the carbonaceous material which permits adsorption, and preferably an increase in the adsorption capacity of the carbonaceous material may be used in the present invention.

Preferably, the organic group attached to the carbonaceous material is an acid or base or 25 a salt of an acid or base, and specific examples include phenyl or naphthyl groups having

substituents like sulfonic acid and carboxylic acid. Quaternary ammonium can also be used. Most preferred organic groups attached to the carbonaceous material are  $(C_6H_4)-SO_3^-Na^+$ ,  $(C_6H_4)-SO_3^-K^+$ ,  $(C_6H_4)-SO_3^-Li^+$ , and the like. Generally, an acid-type organic group attachment will be useful in adsorbing basic adsorbates while a base-type organic group attachment will be 5 useful in adsorbing acidic adsorbates.

Other preferred organic groups which can be used in the present invention include amino acids and derivatized amino acids (e.g., phenyl alanine and its derivatives), cyclodextrins, immobilized proteins and polyproteins, and the like. Other organic groups include, but are not limited to,  $C_6F_5-$  groups and/or trifluoromethyl-phenyl groups, and bis-trifluorophenyl groups, 10 other aromatic groups with fluorine groups, and the like. These organic groups are particularly preferred with respect to the embodiments of the present invention relating to chromatography and other separation techniques.

Other preferred organic groups which are attached onto the carbonaceous material include  $-Ar-(C_nH_{2n+1})_x$  group functionalities, wherein n is an integer of from about 1 to about 30 and x is an integer of from about 1 to about 3. These groups are particularly preferred for 15 purposes of reverse phase chromatography. Another example of an organic group is benzene with a sulfonic group, benzoic groups, isophtalic groups which are particularly useful for cationic exchanges and quaternary amine groups which are particularly preferred for anionic exchanges.

20 Organic groups such as cyclodextrins which are directly attached onto the carbonaceous material or attached through an alkyl group such as  $C_nH_{2n+1}$  chain wherein n is an integer of from about 3 to about 20 and also preferred. Other groups that can be attached are optically pure amino acids and derivatized amino acids, immobilized proteins, and the like. These types of organic groups are particularly preferred with respect to chiral chromatography.

In addition, polyethyleneglycol (PEG groups) and methoxy-terminated PEG groups as well as derivatized PEG and MPEG groups can be attached onto the carbonaceous material. These types of organic groups are particularly preferred with respect to affinity and/or hydrophobic interactions chromatography for the separation, for instance, of proteins and 5 polyproteins.

In addition, the present invention has the ability to attach organic groups such that the organic groups block out microporosity of the carbonaceous material and thus permits the use of microporous materials for separation techniques, such as chromatography. Accordingly, the present invention permits the use of microporous materials that would otherwise not be 10 chromatographically useful for separations.

In the present invention, more than one type of group can be attached onto the carbonaceous material. This is especially useful to fill in any gaps on the surface of the carbonaceous material not having an attached organic group. The filling in of such gaps promotes better selectivity and/or blocks any microporosity that may still exist in the 15 carbonaceous material. Typically, the optional second organic group is attached after the first primary organic group is attached and the modified carbonaceous material is preferably purified is described above by removing any by-products that are produced from attaching an organic group onto the carbonaceous material. Afterwards, the second organic group can then be attached using the same diazonium salt or other attachment methods. Typically, the type of 20 secondary organic groups which are subsequently attached include, but are not limited to, organic groups which are shorter in chain length or have less steric hindrance than the first organic group attached. For instance, preferred secondary organic groups include, but are not limited to, phenyl groups, alkyl phenyl groups having short alkyl chains (e.g., C<sub>1</sub>-C<sub>15</sub>), and the like. Particularly preferred groups include, phenyl, methyl-phenyl, 3,5-dimethyl-phenyl, 4- 25 isopropyl-phenyl, and 4-tert-butyl-phenyl.

The modified carbonaceous materials of the present invention, especially when the attached organic groups are alkyl phenyl groups, like 4-alkyl-phenyl, where the length of the alkyl chain is between 1 and 30, (preferably between 8 or 18), are especially useful for reverse phase chromatography applications having surface properties directly analogous to octadecyl-modified silica. Additionally, the modified carbonaceous materials described above, can have secondary attached groups such as phenyl, methyl-phenyl, dimethyl-phenyl, isopropyl-phenyl, tert-butyl-phenyl, and the like. The carbonaceous materials of the present invention will have one or more of the following properties compared to the conventional octadecyl silica:

- Enhanced pH stability (octadecyl silica is only used in a narrow pH and rarely above pH 8). The enhanced carbonaceous materials of the present invention will be stable at all pH.
- Enhanced temperature stability. These materials can be used at temperatures up to 250°C, preferably up to 200°C without significant degradation in performance.
- Enhanced resistance to swelling.
- The ability to dial-in the surface properties by determining the concentration of active and endcapping groups on the surface, which would give the stationary phase different selectivities.

A combination of different organic groups is possible. For instance, it is within the bounds of the present invention to attach more than one type of organic group to the same carbonaceous material or use a combination of carbonaceous materials, wherein some of the carbonaceous material has been modified with one organic group and another portion of the carbonaceous material has been modified with a different organic group. Varying degrees of modification are also possible, such as low weight percent or surface area modification, or a high weight percent or surface area modification. Also, mixtures of modified carbonaceous material and unmodified carbonaceous material can be used. Mixtures of modified

carbonaceous material with different functionalizations and/or different levels of treatment can be used.

Preferably, the modified carbonaceous materials of the present invention, especially when the attached organic group is a phenyl or naphthyl group having substituents like sulfonic acid, carboxylic acid, or quaternary ammonium or salts thereof, can be directly analogous to polymeric ion exchange resins. These types of carbonaceous materials of the present invention can have one or more of the following properties as compared to conventional polymeric ion exchangers:

- 5 a) higher temperature stability;
- 10 b) greater resistance to swelling; and
- c) greater mechanical strength without adversely affecting uptake kinetics.

Furthermore, the modified carbonaceous materials of the present invention, besides being used as adsorbents, can also be used in separations ranging from water treatment to metals separation/recovery, ion exchange, catalysis, and the like. An additional advantage of an adsorbent possessing exchangeable groups as described above is that it confers on the material 15 the ability to be further surface modified using ion exchange procedures.

With respect to the adsorbates, any adsorbate capable of being adsorbed by one or more of the modified carbonaceous materials of the present invention is contemplated to be within the bounds of the present invention. Examples include, but are not limited to, polar species such as 20 water, ammonia, mercaptans, sulfur dioxide, and hydrogen sulfide. By "polar species," it is understood that this is a species whose electronic structure is not symmetrical. This includes molecules that possess dipole moments, for example  $H_2O$  and  $NH_3$ ; and/or molecules that possess quadrupole moments, such as  $CO_2$  and molecules that possess unsaturated pi bonds ( $\pi$ ), such as alkenes, alkynes, and other organic and inorganic compounds with double and triple 25 bonds. Non-polar species such as argon, oxygen, methane, and the like can also be adsorbed

with the appropriate modified carbonaceous materials of the present invention. In view of the description provided in this application, those skilled in the art will be able to determine which organic groups need to be attached to the carbonaceous materials in order to achieve the most effective adsorption affinity or increase in adsorption, depending upon the adsorbate and the 5 adsorption processes involved.

By developing an adsorbent composition containing a modified carbonaceous material capable of adsorbing an adsorbate, selectivity for a particular adsorbate can be enhanced. Using the proper modified carbonaceous material, one can selectively adsorb particular species from a multicomponent mixture. In other words, modifying the carbonaceous material to create the 10 adsorbent composition of the present invention can decrease adsorption affinity for one component in order to maximize the adsorption affinity of another component which will maximize separation of the second component from the first component. Furthermore, by increasing adsorption of polar species, this further results in the relatively decreased adsorption of nonpolar species which improves selectivity. Further, the carbonaceous material can be 15 modified in such a manner as to add a hydrophobic group to "disable" the oxygen functionalities on the surface of the carbonaceous material to increase the selectivity for the adsorption of nonpolar species.

The adsorbate can be in a liquid phase or in the gaseous or vapor phase, depending upon the needs and desires of the user. Certain adsorbates can be more efficiently adsorbed from the 20 vapor or gaseous phases than from the liquid phase or vice versa, and the modified carbonaceous materials of the present invention are effective in adsorption from either phase.

One advantage of the present invention is to modify the surface of an activated carbon or carbon black adsorbent extensively, without damaging the structure or making the adsorbent more friable. For instance, a carbonaceous material can be surface modified based on the 25 present invention with exchangeable sodium cations attached to the surface. This is very useful

from the point of view of substituting different ions to alter the chemistry of the surface.

The beneficial effect of using the modified carbonaceous materials of the present invention for the purpose of adsorption can be demonstrated by comparing the adsorption isotherms of an adsorbate on an unmodified carbonaceous adsorbent and the same carbonaceous adsorbent modified in accordance with the present invention.

The present invention will be further clarified by the following examples, which are intended to be purely exemplary of the present invention.

## **EXAMPLES**

10 The effectiveness of the surface modification of exemplary carbonaceous material was determined by comparing the adsorption isotherms of various adsorbates on the unmodified carbonaceous materials, with adsorption isotherms on the carbonaceous materials modified in accordance with the present invention. Adsorbates used were water and CO<sub>2</sub>, but other adsorbates could also be used.

15 **Example 1**

Pellets of Black Pearls® 430 carbon black and Darco S51 activated carbon from Norit were surface-modified using the following procedure:

**Surface modification of Black Pearls® 430 Carbon Black:**

20 A dispersion of 5 ml of water dilutable phenol-formaldehyde thermosetting resin (Schenectady International, Schenectady, NY) in 50 mL of water was mixed with 50 g of Black Pearls® 430 carbon black (available from Cabot Corp., Boston, MA). The mixture was pressed in 1 g portions using a 0.25 inch stainless steel die at a pressure of 5000 psi. The pellets were heated under flowing argon at 110°C for one hour and at 135°C for one hour to cure the resin. The temperature was then raised under flowing argon at 20°C/min until a temperature of 650°C 25 was reached. The temperature was then held at 650°C for three hours and cooled under flowing

argon. The pellets were then crushed into pieces about 1 mm by 2 mm.

An aqueous solution of 0.81 g of sodium nitrite in about 1 g of water was added to a mixture of 16.8 g of the carbon black granules, 2.04 g of sulfanilic acid, and 50 g of water that was stirring at 84°C. After stirring for two hours, the resulting material was dried in an oven at 5 65°C.

Surface modification of activated carbon:

An aqueous solution of 30.5 g of sodium nitrite in about 100 g of water was added to a boiling mixture of 130 g of DARCO S51 activated carbon (available from Norit), 76.5 g of sulfanilic acid, and 1300 g of water. After stirring for 15 minutes, the heating was discontinued 10 and the mixture was allowed to cool to room temperature with stirring. The resulting material was dried overnight in an oven at 50°C.

Ion Exchange:

The surface modified carbons were washed with a large amount of deionized water and dried. The material thus obtained was in the sodium form. Further modification of the carbon 15 into potassium and lithium forms was carried out by ion exchange using 2M solutions of KOH and LiOH, respectively. The ion-exchanged material was washed thoroughly and dried. Adsorption experiments were carried out on the washed, dried materials.

The surface areas of the unmodified and surface modified carbon materials are shown in Table 1 below. Surface areas were calculated from nitrogen (77 K) adsorption data using the 20 BET formalism (S.J. Gregg and K.S.W. Sing, in Adsorption, Surface Area, and Porosity," Academic Press, 1982). The adsorption experiments were carried out on an ASAP 2000 automated instrument, manufactured by Micromeritics Corp.

**Table 1: Surface Areas and Pore Volumes of Unmodified and Surface Modified Materials**

Sample ID	BET Surface Area, m <sup>2</sup> /g	Pore Volume, cm <sup>3</sup> /g
BP 430 pellets, unmodified	99	0.518
BP 430, modified, washed	92	0.49
Darco S51	694	0.809
Darco S51, modified, washed	141.3	0.279

5 While the activated carbon lost some surface area and pore volume after the surface modification treatment, both the carbon black and the activated carbon underwent an increase in adsorption capacity per unit surface area as a result of the surface modification. The loss of any surface area and pore volume may be mitigated by pre-treating the carbonaceous material with immiscible organic solvent, like heptane. The results from adsorption of water vapor at 298 K  
10 on the unmodified and modified material are shown in Figure 1 (carbon black) and Figure 2 (activated carbon). The water adsorption experiments were carried out by a batch technique that involved equilibrating the sample with water vapor at a constant relative humidity, in a sealed cell. The constant relative humidities were attained by using saturated salt solutions, which have known relative humidities above their surface.

15 Both the activated carbon and carbon black contained Na<sup>+</sup> ions on the surface after the surface modification was carried out. The Na<sup>+</sup> ions can be substituted by other ions using standard ion exchange procedures (e.g., *see Ion Exchange*, by F. Helfferich, McGraw-Hill, 1962). The water adsorption isotherms for the surface-modified material with Na<sup>+</sup> ions on the surface, as well as the other ionic forms derived by ion exchange, are shown in Figures 1 and 2.  
20 The adsorption isotherms show the quantity of water vapor adsorbed, per gram of adsorbent, as a function of the relative pressure of water vapor. Figures 3 and 4 show the same data normalized by the BET surface area of the materials. It is clear that the adsorption capacities

per unit area of the carbon black, Black Pearls® 430 carbon black and the Darco S51 carbon black, are considerably enhanced by the surface modification described in this invention. In addition, the shape of the water adsorption isotherm is changed as a result of the surface modification (concave upward, to linear or convex upward).

5 The surface modification technique of the present invention may affect the adsorption of gases like CO<sub>2</sub> as well, which possesses a quadrupole movement. Figure 5 shows the adsorption isotherm of CO<sub>2</sub> from the gas phase at 273 K on the same unmodified and modified Black Pearls® 430 carbon black. Adsorption of CO<sub>2</sub> was carried out on an ASAP 2000 automated adsorption system manufactured by Micromeritics Corp. The figure shows the quantity of CO<sub>2</sub> adsorbed as a function of the CO<sub>2</sub> pressure. Clearly, the adsorption of CO<sub>2</sub> is enhanced by the carbon surface modification technique described in this invention.

10

15 Example 2

The use of carbonaceous material for chromatographic and other biochemical applications involving contact with proteins has traditionally been hindered by the non-specific adsorption of proteins at the carbon surface. Using various types of conventional carbonaceous materials as well as carbonaceous materials of the present invention, several experiments were conducted to determine the non-specific adsorption of proteins at the carbon surface by these various carbonaceous materials including carbonaceous materials of the present invention.

20 Black Pearls® 3700, available from Cabot Corporation, was chemically modified by attaching methoxy terminated polyethylene glycol groups onto the carbon black with the use of the diazonium reaction described above. The polyethylene groups attached had average molecular weights of 350, 750, and 2000. The modified carbon blacks were dispersed in water during their preparation and subsequently purified by 10 volumes of diafiltration for removal of impurities and reaction byproducts. A stock solution of 10 mg/ml of Bovine Serum Albumin (BSA) was

25 prepared and used for all the experiments detailed below. Appropriate amounts of dispersion

containing 0.5 g of each modified carbon black and 0.5 g of unmodified BP3700 were introduced in separate 20 ml vials. In each vial, protein solution and deionized water were introduced so that the total final weight of the contents of each vial was approximately 7.5 g, with approximately 7 ml of liquid. Protein solutions varied in concentrations between 0 and 4.5 mg/ml. The vials were vortexed for 2 hours to intimately mix the protein solution with the carbon black particles. After 1 week, the vials were vortexed again, and subsequently 2 ml aliquots were taken and centrifuged at 11,000 RPM for the time required to separate the carbon black particles. The protein concentrations in the supernatant solutions were measured using the standard Bradford assay. The protein concentrations were measured using the standard Bradford Assay as described in *Analytical Biochemistry*, 72, pp. 248-254 (1976), which is incorporated in its entirety by reference herein. As a comparison, Black Pearls® 3700 which was not modified was used as a control. The remaining concentration of BSA in the aqueous solution was measured every day for 1 week and the amount of BSA adsorbed by the various carbonaceous materials in the separate experiments was plotted. As can be seen in Fig. 6, the modified carbonaceous material of the present invention was quite successful in not adsorbing the protein since the diagonal line in Fig. 6 represents no adsorption and as can be seen, the chemically modified carbonaceous materials of the present invention were quite successful in not adsorbing significant amounts of proteins on the surface. However, the untreated or conventional carbon black adsorbs significant amounts of the BSA on the carbon surface. Thus, the present invention, through the use of organic groups on a carbonaceous material can be quite successful in promoting non-specific adsorption of protein at the carbon surface. The conventional carbon black adsorbed approximately  $0.9 \text{ mg/m}^2$  of BSA from a solution after one week while the concentration of BSA in the aqueous solution did not change in the presence of the carbonaceous materials of the present invention.

Other embodiments of the present invention will be apparent to those skilled in the art from consideration of the specification and practice of the invention disclosed herein. It is intended that the specification and examples be considered as exemplary only, with a true scope and spirit of the invention being indicated by the following claims.

**WHAT IS CLAIMED IS:**

1. A chromatography column comprising a column having a stationary phase and a mobile phase, wherein said stationary phase comprises carbonaceous material having attached at least one organic group.
- 5 2. The chromatography column of claim 1, wherein said organic group comprises at least one aromatic group directly attached onto the carbonaceous material.
3. The chromatography column of claim 1, wherein said organic group comprises at least one alkyl group directly attached onto the carbonaceous material.
4. The chromatography column of claim 1, further comprising a substance  
10 comprising chemical species to be separated in said column.
5. A separation device comprising a mobile phase and a stationary phase, wherein said stationary phase comprises carbonaceous material having attached at least one organic group.
6. A method for conducting separation of chemical species from a substance,  
15 wherein said method comprises passing said substance through a system containing a mobile phase and a stationary phase, wherein said stationary phase comprises carbonaceous material having attached at least one organic group.
7. The method of claim 6, wherein said separation is chromatography.
8. The method of claim 6, wherein said separation is size exclusion  
20 chromatography.
9. The method of claim 6, wherein said separation is chromatography by affinity wherein the chemical species in the substance have different affinities for the stationary phase.
10. The method of claim 6, wherein said separation is an adsorption-desorption chromatography.
- 25 11. The method of claim 6, wherein said separation is electrophoresis.

12. A method for conducting separation by electrophoresis comprising a stationary phase and a mobile phase located between a positive electrode and a negative electrode, passing a current between said electrodes, and introducing a substance containing different chemical species to be separated, wherein said stationary phase comprises carbonaceous material having attached at least one organic group.

5

13. A membrane separation system comprising a membrane wherein said membrane comprises carbonaceous material having attached at least one organic group.

14. The membrane separation system of claim 13, wherein said system is a reverse osmosis system.

10

15. An electrophoresis separation comprising a stationary phase, a mobile phase, and a positive electrode and a negative electrode, wherein said stationary phase comprises carbonaceous material having attached at least one organic group.

16. The separation device of claim 5, wherein the organic group is a phenyl or naphthyl group having ionic or ionizable groups.

15

17. The separation device of claim 5, wherein the organic group comprises an amino acid or derivatized amino acid, cyclodextrin, immobilized protein, polypeptides, or combinations thereof.

18. The separation device of claim 5, wherein the organic group comprises a  $-C_6F_5$  group, a trifluoromethyl-phenyl group, a bis-trifluorophenyl group, or combinations thereof.

20

19. The separation device of claim 5, wherein the organic group comprises  $-Ar-(C_nH_{2n+1})_x$  group, wherein n is an integer of from about 1 to about 30 and x is an integer of from about 1 to about 3.

20. The separation device of claim 5, wherein the organic group comprises cyclodextrin attached through an alkyl group.

21. The separation device of claim 5, wherein the organic group comprises polyethylene glycol or methoxy-terminated polyethylene glycol or derivatized resins thereof.

22. The separation device of claim 5, wherein the organic group comprises -Ar- $((C_nH_{2n})COOX)_m$ , wherein Ar is an aromatic group, n is 0 to 20, m is 1 to 3, and X is H, 5 a cation, or an organic group.

23. The separation device of claim 5, wherein the organic group comprises Ar- $((C_nH_{2n})OH)_m$ , wherein Ar is an aromatic group, n is 0 to 20, m is 1 to 3.

24. The separation device of claim 5, wherein the organic group comprises -Ar- $((C_nH_{2n})NH_2)_m$ , wherein n is 0 to 20, m is 1 to 3, or its protonated form: -Ar-  
10  $((C_nH_{2n})NH_3X)_m$ , wherein X is an ion, and Ar is an aromatic group.

25. The separation device of claim 5, wherein the organic group comprises -Ar- $((C_nH_{2n})CHNH_3^+COO^-)_m$  and the reaction products thereof with molecules containing functional groups terminated in -NH<sub>2</sub>, -OH, or -COOH, wherein Ar is an aromatic group and n is 0 to 20.

15 26. The separation device of claim 5, wherein the organic group comprises -Ar- $((C_nH_{2n})CH=CH_2)_m$ , wherein n is 0 to 20, m is 1 to 3 or -Ar- $((C_nH_{2n})SO_2CH=CH_2)_m$ , where n is 0 to 20 and m is 1 to 3.

27. The separation device of claim 5, wherein the organic group comprises at least one chiral ligand group.

20 28. The separation device of claim 16, further comprising a second organic group attached on the carbonaceous material.

29. The separation device of claim 17, further comprising a second organic group attached on the carbonaceous material.

30. The separation device of claim 18, further comprising a second organic group attached on the carbonaceous material.

31. The separation device of claim 19, further comprising a second organic group attached on the carbonaceous material.

5 32. The separation device of claim 20, further comprising a second organic group attached on the carbonaceous material.

33. The separation device of claim 21, further comprising a second organic group attached on the carbonaceous material.

10 34. The separation device of claim 22, further comprising a second organic group attached on the carbonaceous material.

35. The separation device of claim 23, further comprising a second organic group attached on the carbonaceous material.

36. The separation device of claim 24, further comprising a second organic group attached on the carbonaceous material.

15 37. The separation device of claim 25, further comprising a second organic group attached on the carbonaceous material.

38. The separation device of claim 26, further comprising a second organic group attached on the carbonaceous material.

39. The separation device of claim 28, wherein said second organic group has a 20 shorter chain length or less steric hindrance than said organic group.

40. The separation device of claim 29, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

41. The separation device of claim 30, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

42. The separation device of claim 31, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

43. The separation device of claim 32, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

5 44. The separation device of claim 33, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

45. The separation device of claim 34, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

10 46. The separation device of claim 35, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

47. The separation device of claim 36, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

48. The separation device of claim 37, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

15 49. The separation device of claim 38, wherein said second organic group has a shorter chain length or less steric hindrance than said organic group.

**ABSTRACT OF THE DISCLOSURE**

Separation devices and systems are described which have a stationary phase and a mobile phase, wherein the stationary phase contains carbonaceous material having attached at least one organic group. The stationary phase which is used in the present invention has the 5 ability to dial in the selectivity by attaching the proper organic groups onto the carbonaceous material in order to achieve the desired separation. Various separation processes are described such as chromatography, electrophoresis, magnetic separations, membrane separations, and the like. The processes to accomplish these types of separations are also described.

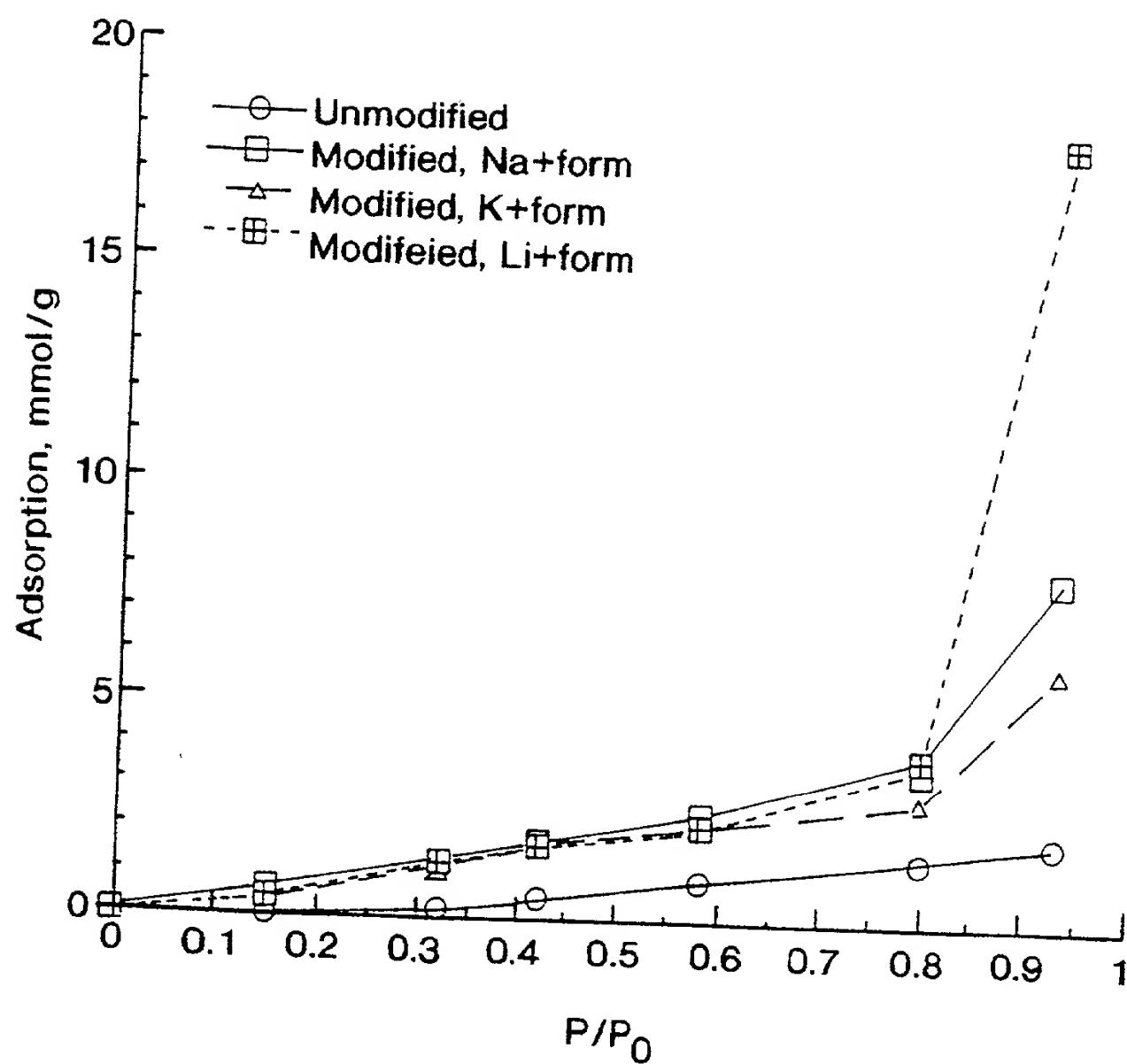


FIG. 1

2 / 5

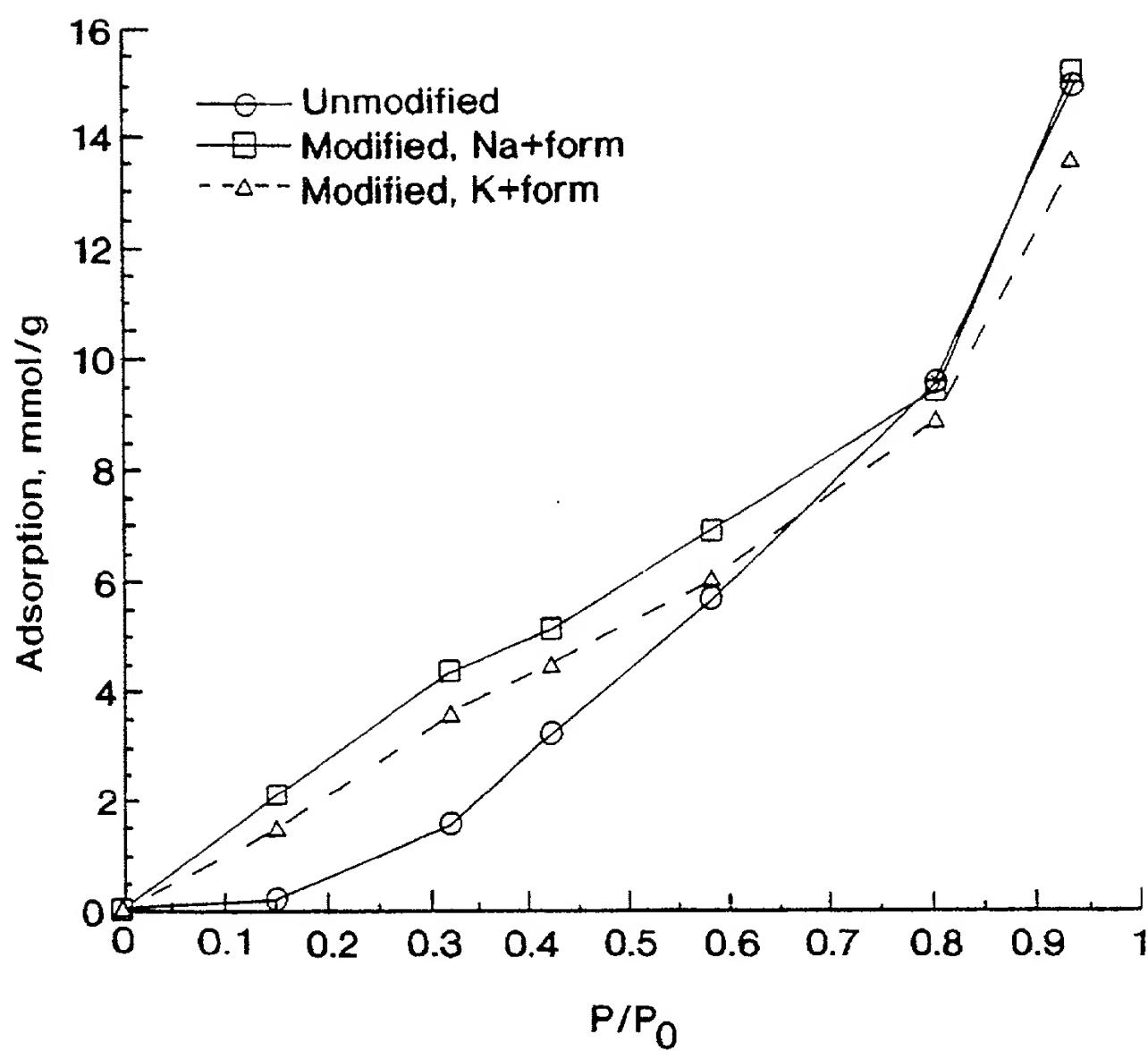


FIG. 2

SUBSTITUTE SHEET (RULE 26)

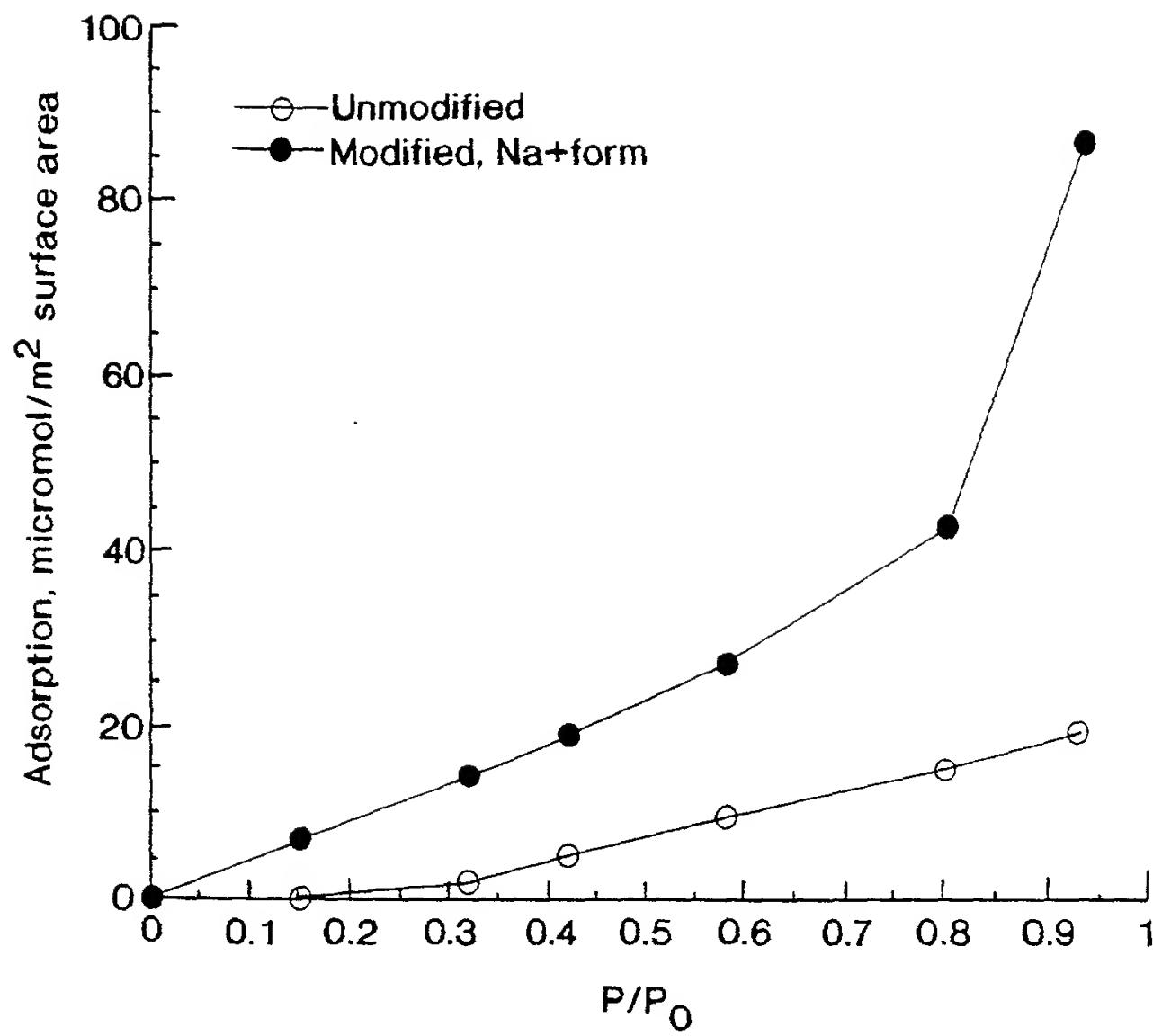


FIG. 3

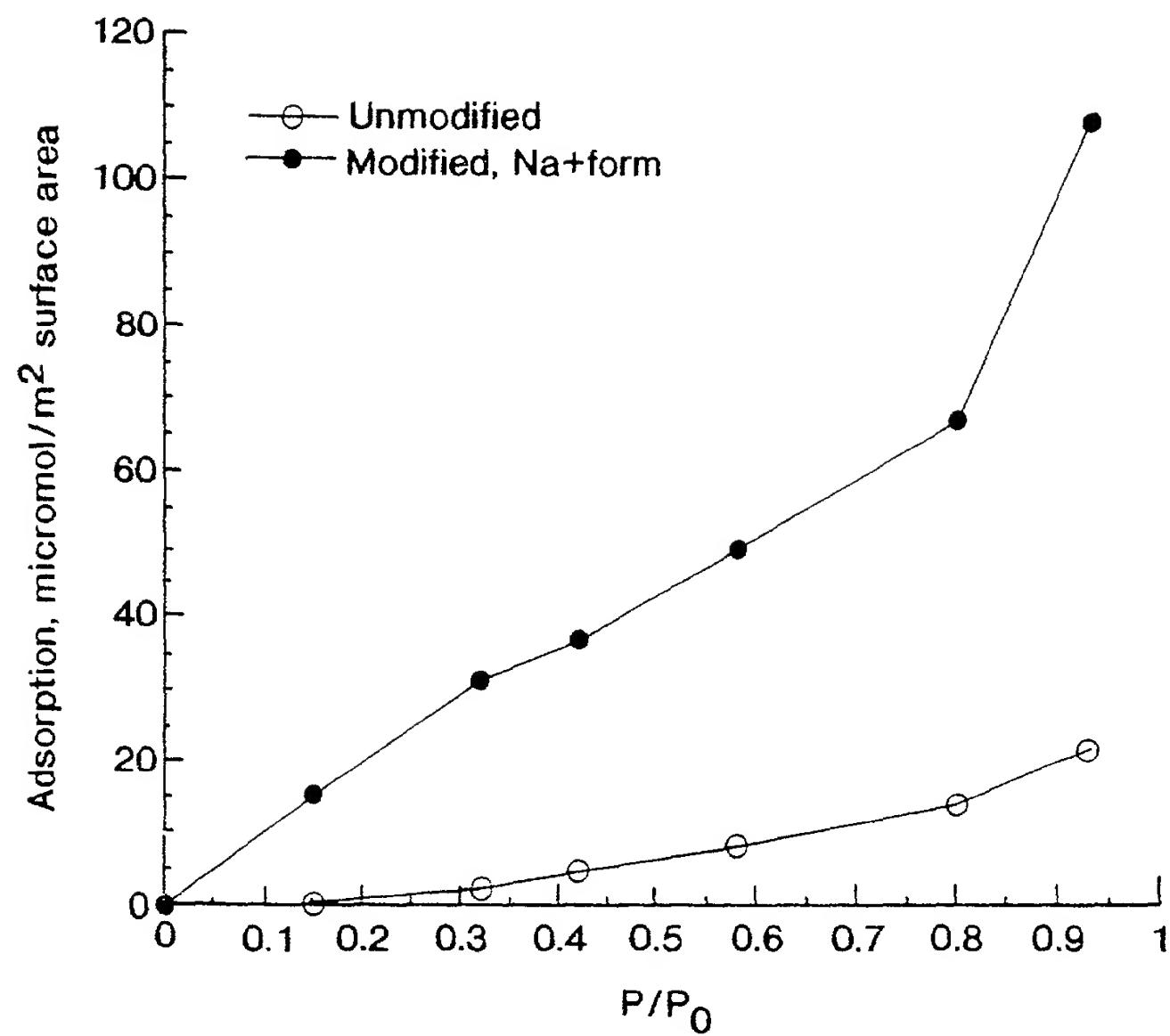


FIG. 4

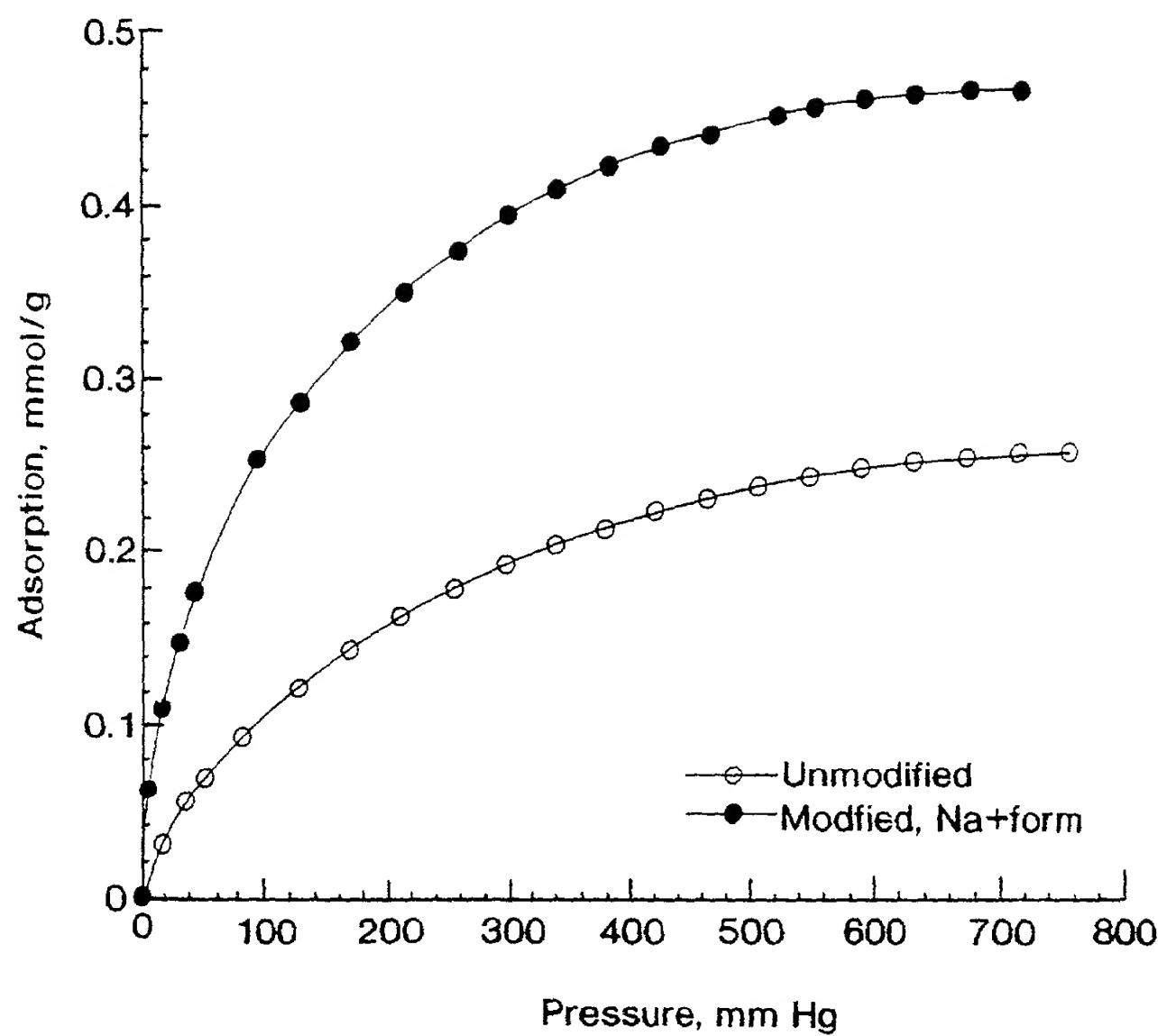


FIG. 5

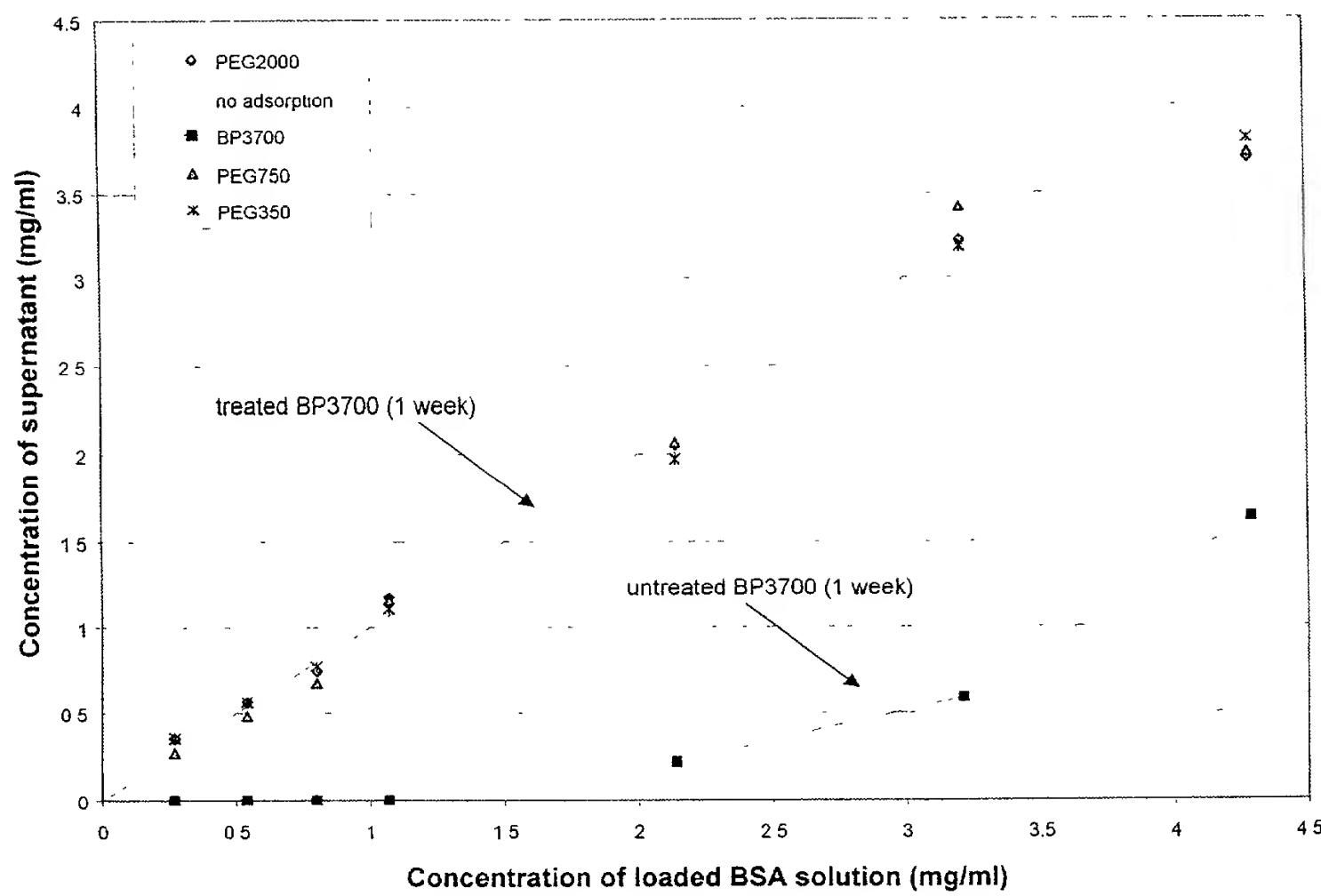


FIG. 6